

alluded to is that described in the previous quotations, it is not a little remarkable that Mr. Lockyer's experiments should so "entirely endorse" what Watts himself has shown to have been in part erroneous.

Lastly, we cannot allow Mr. Lockyer's assertion that Ångström and Thalèn's conclusions "rest more upon a theory which has been shown to be false since the labours commenced, and analogy, than upon experiment," to remain uncorrected. Their conclusions are eminently inductions from experiments carried on, as they say, during several years, of which the most important are particularly described. Many of the experiments which led up to their conclusions had been previously published by Thalèn in 1866 ("Årsskrift, Upsala"), in a paper in which he correctly described and distinguished the spectra of hydrocarbons, of oxide of carbon, and of carbon respectively, and besides described the spectrum of the spark between carbon poles in nitrogen. This paper is an admirable sample of good experimental work, and its perusal, together with the later paper of 1875, leaves no doubt that, whatever theories they may have held, Ångström and Thalèn relied mainly on experiment and observation to prove the soundness of their conclusions.

In conclusion, Mr. Lockyer introduces a reference to a former work of ours on the magnesium-hydrogen spectrum, and to a theoretical deduction regarding the interactions which might produce the cometic spectrum, making the following remark:—

"From what I have shown it will be clear that the consequences drawn in the following paragraphs by Messrs. Liveing and Dewar from the assumed hydrogen-carbon bands are entirely invalid."

As this opens out a question entirely beside that in hand, depending on the validity of the premises from which Mr. Lockyer draws his conclusion, we prefer to deal with it when we discuss, in our next paper, the spectra of carbon compounds and the experimental evidence Mr. Lockyer has adduced in support of such assertions.

VI. "On the Spectra of the Compounds of Carbon with Hydrogen and Nitrogen. No. II." By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received May 27, 1880.

In our last communication on this subject (*ante*, p. 152), we thus summarised the results of our observations as to the "nitrocarbon spectrum."*

* In using this term we merely mean that we are dealing with a spectrum invariably associated with the presence of nitrogen and carbon in such conditions that chemical union takes place, without any reference to the particular compound produced.

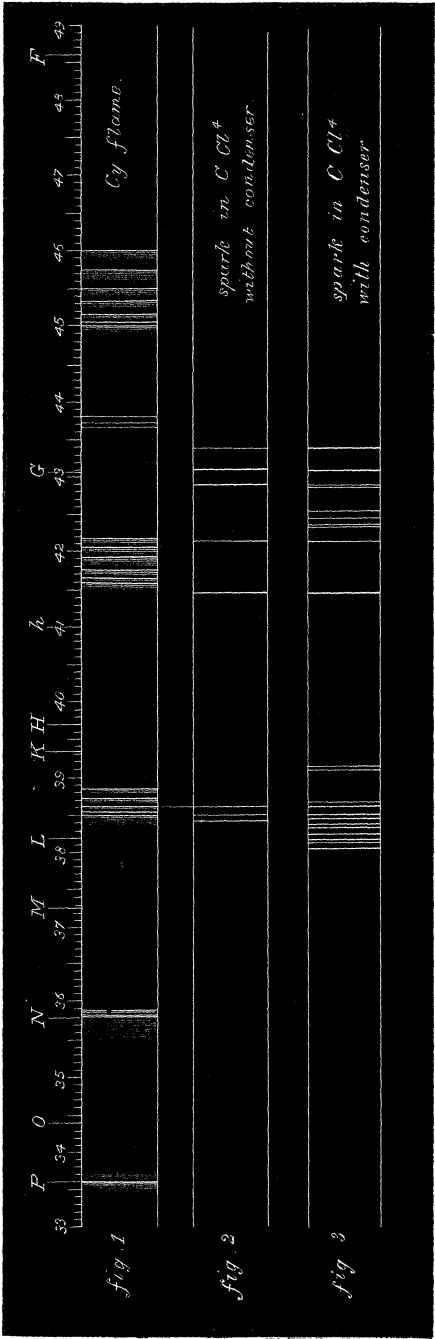
"On a review of the whole series of observations, certain points stand out plainly. In the first place, the seven blue, the violet, and ultra-violet bands, characteristic of the flame of cyanogen, are conspicuous in the arc taken in an atmosphere of nitrogen, air, nitric oxide, or ammonia, and they disappear, almost, if not quite, when the arc is taken in a non-nitrogenous atmosphere of hydrogen, carbonic oxide, carbonic acid, or chlorine.* These same bands are seen brightly in the flames of cyanogen and hydrocyanic acid, but are not seen in those of hydrocarbons, carbonic oxide, or carbon disulphide. The conclusion seems irresistible that they belong to cyanogen; and this conclusion does not seem to us at all invalidated by the fact that they are seen weakly, or by flashes, in the arc or spark taken in gases supposed free from nitrogen, by reason of the extreme difficulty of removing the last traces of air. They are never, in such a case, the principal or prominent part of the spectrum, and in a continuous experiment they are seen to fade out in proportion as the nitrogen is removed. This conclusion is strengthened by the observations of one of us, that cyanogen (or hydrocyanic acid) is generated in the arc in atmospheric air in large quantity."

The observations and experiments which we have since made all tend to confirm the correctness of the foregoing induction, while they help to remove the apparent inconsistency of some recorded observations with our conclusions. More particularly they explain the appearance of the bands which we, in common with Ångström and Thalén, have ascribed to a compound of carbon with nitrogen, in some cases in which nitrogen had been supposed to be absent, by showing the sensibility of the spectroscopic test for nitrocarbon compounds under varied circumstances, and the consequent necessity for something more than ordinary care in the preparation of materials and conduct of experiments, if inferences dependent on the presumed absence of nitrogen (or hydrogen, as the case may be) are to be drawn from them.

The Flame of Cyanogen.

The accompanying diagram (fig. 1) shows approximately the relative position of the bands in that part of the spectrum of the flame of cyanogen fed with a jet of oxygen which is more refrangible than the Fraunhofer line F. Only those bands which are less refrangible than the solar line L have been before described, but photographs show another set of two shaded bands slightly less refrangible than the solar line N accompanied by a very broad diffuse band of less intensity on the more refrangible side of N; also a strong shaded band, which appears to be absolutely coincident with the remarkable shaded

* We have repeated and confirmed the experiments with the De Meritens arc in different gases. The arc examined in different *fluids* also supports the original conclusions.



band in the solar spectrum, which has been designated by the letter P; and near this, on the more refrangible side, a much fainter diffuse band, which also seems to coincide with a part of the solar spectrum sensibly less luminous than the parts on either side of it. This spectrum is remarkably persistent at all temperatures of the flame. Watts found that it did not disappear when the flame was cooled down as much as possible by diluting the cyanogen with carbonic acid; and we have found that it retains its characters when the cyanogen is burnt in nitric oxide. The flame in the last case must be one of the hottest known, from the large amount of heat evolved in the decomposition of cyanogen and nitric oxide, namely, 74,500 and 43,300 units per molecule respectively. There is in the case of cyanogen, as in the case of so many other substances, a difference in the relative intensities of the different parts of the spectrum of the flame at different temperatures, but no other change of character; and we are unable to confirm the observation of Watts, that cyanogen burning in oxygen gives only the bands which we assign to hydrocarbons. It is true, that in the upper part of the flame where much or all of the cyanogen is oxidised or decomposed the spectrum is continuous, but at the base of the flame where it is issuing from the nozzle we have always seen the nitrocarbon bands, both when the cyanogen is burning in oxygen and when it is burning in nitric oxide.

On the theory that these groups are the product of an exceptional temperature in the case of the cyanogen flame, it is inconceivable that they could disappear by combustion in oxygen, instead of in ordinary air. Our observations accord with the statement of Morren, Plücker, Hittorf, and Thalén, that a cyanogen flame, fed with oxygen, when it is intensely luminous, still yields these peculiar groups. We have found these peculiar groupings in the flame when it had a current of oxygen in the middle, and was likewise surrounded outside with oxygen. There is nothing remarkable in observing only a continuous spectrum from any hydrocarbon or nitrocarbon by using excess of oxygen, as we know from Frankland's experiments that carbonic acid and water vapour at the high temperature of flame under compression gives a continuous spectrum. In fact, this is what we should anticipate, provided intermediate, and not the final, compounds are the active sources of the banded spectrum.

Each of the five sets of bands shown in the diagram is attended on its more refrangible side by a series of rhythmical lines extending to a considerable distance, not shown in the diagram, but easily seen in the photographs.

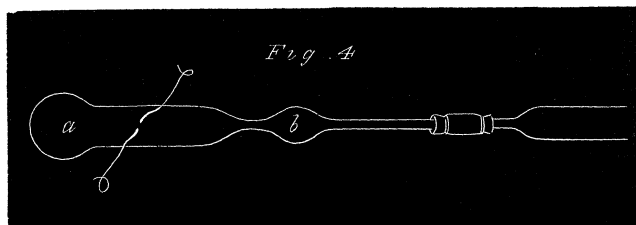
Coal gas burning in oxygen gives no bands above that near G within the range of the diagram, fig. 1, nor are the visible cyanogen bands seen in the flames of many organic compounds containing combined nitrogen; but beyond this our photographs show a spectrum

of a character quite different from that at the less refrangible end. The most remarkable part of this spectrum is a long series of closely set strong lines, filling the region between the solar lines R and S, and ending abruptly with two strong lines a little beyond S. These are lines of various intensities, not regularly arranged so as to give shaded bands like those in the less refrangible part of the spectrum. Beyond these lines there is another large group of lines, not so strong or so closely set, but sharp and well defined. It will be a work of time to examine in detail this very striking and peculiar spectrum; at present we can only indicate its general character. We are not yet sure whether it is produced by pure hydrocarbons, or may not be due to impurities such as sulphur in the coal gas.*

Spark Discharge in Carbon Tetrachloride.

We have conducted the experiments with carbon tetrachloride with great care, and numerous repetitions on account of the prominence given to an experiment with this compound by Mr. Lockyer in a recent "Note on the Spectrum of Carbon," communicated to the Society, and because our results in every case differ from those which he obtained.

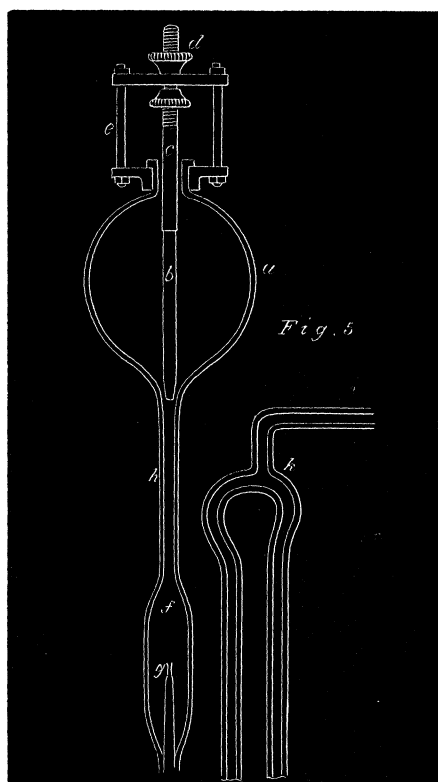
The form of sparking tube employed was similar to that used by Salet, and is shown in the annexed diagram, fig. 4. This was attached



by thick rubber tubing to a straight glass tube of which one half, about 6 inches long, was filled with phosphoric anhydride, and the other half with small fragments of soda-lime to prevent any chlorine from the decomposition of the tetrachloride by the spark from reaching the pump. The pump was connected by rubber tubing to that end of the tube which contained soda-lime. The tetrachloride used had been prepared in our own laboratory from carbon disulphide, and fractionated until it had a constant boiling point of 77° C. Sufficient of it was introduced into the sparking tube to fill nearly one quarter of the bulb at the end, and the whole interior of the tube thoroughly wetted with it in order to facilitate the removal of the last traces of air.

* Since this passage was written we have found reason to believe that this remarkable spectrum is due not to any carbon compound, but to water. As this takes it beyond the scope of the present paper, we purpose dealing with it hereafter in a separate communication. June 8, 1880.

The Sprengel pump employed differs slightly from those in common use. The reservoir is a globe funnel (*a*, fig. 5), and the valve formed by a glass rod (*b*) with a conical termination ground into the neck of the funnel. This rod at its upper end passes into an iron ferule (*c*), which, by means of a screw and a small frame fixed at the top of the globe, can be raised or lowered at pleasure. A little below the globe the tube expands, and the lower part of the tube enters this expansion,



and terminates upwards in a narrow tube of platinum, round which the glass is fused. By this means the mercury is continually drawn from the centre of a mass of mercury, and there is less chance of air descending with it. Moreover, as the exhaustion proceeds the part of the tube *h*, above the level of the fall *k*, becomes vacuous, and is an effectual trap for any air which may be sucked down with the mercury from the globe. The necessity for such a trap is apparent, for when the pump has been in continued use for two or three days there is always a small bubble of air collected in *h*.

When the tube containing the tetrachloride had been so far exhausted that little but condensible vapours were pumped out, the bulb was heated so as to fill the apparatus with vapour of tetrachloride, the pump still going, and this was repeated as long as any incondensable gas was extracted. Sparks were then passed through the tube for a short time, the pump still being kept going. After a short time it was unnecessary to keep the pump going, as all the chlorine produced by decomposition of the tetrachloride was absorbed by the soda-lime. On now examining the spectrum, no trace of any of the bands we ascribe to nitrocarbons could be detected, either by the eye or by photography, however the spark might be varied. The violet lines of chlorine described by Salet were more or less visible, coming out brightly when a condenser was used. Several tubes were treated in this way, and many photographs taken, but always with the same result; no trace appeared of either the seven blue, the six violet, the five ultra-violet, or of the still more refrangible bands of the cyanogen flame. It is true that all the photographs showed three lines in the ultra-violet, but these do not at all closely resemble the nitrocarbon bands, they are not shaded like the nitrocarbon bands. The least refrangible of the three is coincident with the middle maximum in the ultra-violet set of five bands, but the other two do not coincide with other of these maxima. When a condenser is used these three lines come out with much greater intensity, and two other triplets appear on the more refrangible side, as well as other lines. In order to compare the positions of these lines with the cyanogen bands, we have taken several photographs of the spark in tetrachloride simultaneously with a cyanogen flame, the latter being thrown in by reflexion in the usual way. Wratten and Wainwright's instantaneous dry plates were used, and gave a strong picture of the cyanogen flame after three seconds' exposure, but in order to ensure getting a picture of all the lines which the spark could produce, we gave an exposure of three minutes to the spark. Not one of many photographs so taken showed any traces of the cyanogen bands. The general character of the violet part of the spectrum of the spark in carbon tetrachloride taken without a condenser, but not the exact position to scale of wave-lengths of all the lines, is shown in Diagram 1, fig. 2. Fig. 3 of the same diagram shows the brightest of the additional lines which come out with the use of a condenser. Photographs of sparks taken in hydrochloric acid showed a precisely similar group of ultra-violet lines, so that we have no doubt that the three lines which our photographs show amongst the five ultra-violet nitrocarbon bands are due to chlorine.

A bulb tube was next partly filled with tetrachloride, the end drawn out to a long narrow neck, and the tetrachloride boiled out in an oil-bath (150° C.) so as to expel all air, and the tube sealed off. This tube likewise showed no nitrocarbon bands.

A bulb was then blown in the middle of a piece of narrow glass tubing, and platinum wires sealed into it; some carbon tetrachloride was introduced into the bulb, and a current of hydrogen passed through the tube at atmospheric pressure; when the air was judged to be expelled sparks were passed by means of the wires in the bulb, but no nitrocarbon bands could be detected. In this case the rapid deposit of carbon soon brought the observations to a close, but the result was the same as before.

Solid trichloride was next tried. It was introduced into a tube similar to that described above in the first experiment with tetrachloride, and treated as the tetrachloride had been, the trichloride being mostly sublimed over into the small bulb shown in fig. 4, *b*. The trichloride was found to behave as far as the spectrum is concerned very much as the tetrachloride had done. It gave no nitrocarbon bands at all.

Having satisfied ourselves by repeated trials that pure carbon chloride if free from nitrogen does not give any of the bands we ascribe to nitrocarbon compounds, our next step was to determine whether the addition of nitrogen would bring them out, and if so what quantity of nitrogen would make them visible. For this purpose we first loosened the binding of the rubber tube connecting to the pump a sparking tube containing tetrachloride, and found to give no nitrocarbon bands, and, after letting in very little air, immediately closed it again. On now passing the spark the six violet bands at once appeared, and soon became quite bright, the seven blue bands were not seen immediately the air was admitted, but they too were in a short time well seen.

After trying some other experiments of a similar kind which indicated that a very small quantity of nitrogen was sufficient to develop the nitrocarbon bands in one of these tubes, we introduced a minute fragment of bichromate of ammonia, carefully weighed, and wrapped in platinum foil, into the neck of one of the sparking tubes containing carbon tetrachloride, connected the tube to the Sprengel pump, and removed the air as before. On examination of the spark with the spectroscope no trace of any nitrocarbon band could be detected. A pinch-cock was now put on the rubber tube, and the bichromate was heated by a spirit lamp to decomposition (whereby it is resolved into nitrogen, water, and oxide of chromium). On now passing the spark the six violet bands were well seen. There was no change in the condition of the coil or rheotome, so that the spark was of the same character as it had been before when no nitrocarbon bands were visible, and the change in the spectrum cannot be attributed to any change in the spark. The weight of the bichromate was between $\cdot 0005$ and $\cdot 0006$ gram.; and the nitrogen this would evolve would fill just about $\frac{1}{20}$ of a cubic centimeter at atmospheric pressure. The tube held 30 cub.

centims., so that vapour of carbon tetrachloride when mixed with $\frac{1}{600}$ part of its volume of nitrogen, gives under the action of the electric spark the nitrocarbon bands distinctly. Other similar experiments confirmed this result. It is worthy of remark that the nitrocarbon bands were not seen instantaneously on the admission of nitrogen into the tube, but were gradually developed, as if it was necessary that a certain quantity of nitrocarbon compound should be formed under the influence of the electric discharge and accumulated before its spectrum became visible.

Spark Discharge in other Compounds of Carbon.

Some carbon bisulphide was introduced into another tube, which was drawn out to a long narrow neck, and the carbon bisulphide boiled out in an oil-bath at 200° C., and the tube sealed off. In the spectrum of the spark taken in this tube no nitrocarbon bands, either blue or violet, could be detected however the discharge was varied.

A similar tube, containing benzol and similarly treated, showed no trace of the nitrocarbon bands.

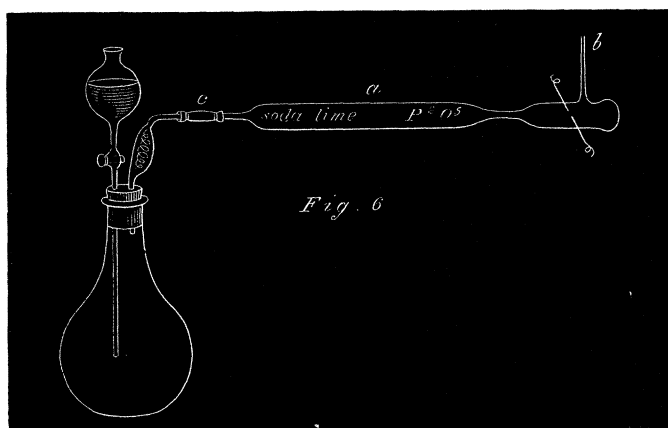
Another tube, containing naphthaline, previously well washed with dilute sulphuric acid, dried and resublimed, was attached to the Sprengel pump, and treated as the tubes with tetrachloride had been. The spark in this tube likewise showed no nitrocarbon bands. After a time the tube cracked, and then the nitrocarbon bands made their appearance, and on setting the pump going a good deal of gas was pumped out. When the air had again been pretty completely exhausted, the nitrocarbon bands no longer showed, but gradually reappeared again as air leaked through the crack. Another tube, containing a mixture of naphthaline and benzol, showed no trace of the nitrocarbon bands.

The observation of the nitrocarbon bands in the spectrum of the spark in naphthaline was one of the reasons which led Watts at one time to ascribe these bands to carbon only. Naphthaline is not well adapted to be the subject of a test experiment in this case, for, from its mode of preparation, it is liable to be contaminated with nitrogenous bases; and the tension of its vapour at ordinary temperatures is so small that, unless the supply is kept up by heating the tube, the spark soon so far decomposes it that the spectrum is reduced to that of hydrogen only. It appears, however, from our experiments, that if the naphthaline is sufficiently purified and freed from air it does not furnish the nitrocarbon spectrum.

As Watts laid much stress on the occurrence of the nitrocarbon bands in the spectrum of the spark taken in carbonic oxide at atmospheric pressure, though they do not appear in carbonic oxide at reduced pressures, as a proof that these bands were due to carbon only,

we have made a series of careful experiments with carbonic oxide at atmospheric pressures.

In our first experiments with this substance the gas was made by the action of sulphuric acid on dried formiate of sodium. The dried formiate was placed in a flask (fig. 6) fitted with a rubber stopper, through which passed the tube of a globe funnel, with a stop-cock for the admission of the sulphuric acid, and an exit tube for the gas. The latter was plugged with asbestos to catch any liquid drops which might be thrown up, and was connected by a thick rubber tube to a tube of the form shown in fig. 6. That part of this tube marked *a* was filled, one-half with soda-lime to catch acids, and the other half with phosphoric anhydride to catch moisture; the gas, after passing through this tube, was burnt as it issued from the narrow opening at *b*.



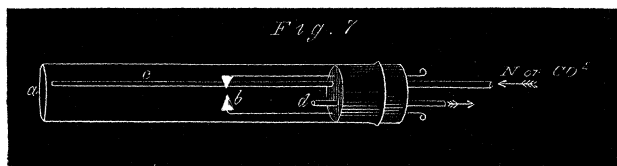
The spectrum of the spark was observed through the small bulb blown on the end. The sulphuric acid was introduced gradually through the funnel, and the stream of gas allowed to pass through the tube for a long time. Sparks were passed between the wires, and the spectrum observed from time to time. At first the six violet bands were well seen, and the seven blue bands faintly; but gradually, as the air became more completely expelled, the blue bands disappeared entirely, and then the violet bands so far died out that it was only by manipulating the coil that they could be made visible, and then only very faintly indeed. A bubble of air, estimated by the length of the tube it filled to be about $\frac{1}{400}$ of the volume of gas in the flask and tube, was now introduced through the funnel, and almost immediately the bands reappeared brightly. As the stream of gas however continued, they again gradually died away until they were represented only by a faint haze. It was subsequently found that each introduction of fresh

acid into the flask was attended with a marked increase in the brightness of the nitrocarbon bands, which died away again when the current of gas was continued without fresh introduction of acid. On testing the acid it was found to contain, as is frequently the case with sulphuric acid, a small quantity of oxides of nitrogen. This quantity was, however, so small that the amount of nitrogen introduced at each introduction of acid must have been but a small portion of the amount introduced in the bubble of air above mentioned, yet it gave a very sensible increase in the brightness of the nitrocarbon bands. The difficulty of getting all the air expelled from the apparatus led us next to adopt a modification of this experiment. The carbonic oxide was generated by heating in a tube of hard glass in an ordinary combustion furnace a mixture of pure and dry potassium oxalate with one quarter of its weight of quicklime, the mixture having been previously heated for some time so as to expel traces of ammonia. The rest of the apparatus was similar to that used in the previous experiment, but in order to expedite the removal of the air the narrow tube, *b*, was connected with a Sprengel pump, and the air exhausted before heating the oxalate. The distant end of the tube with the oxalate was then heated, and the whole apparatus filled with carbonic oxide; it was then again exhausted with the pump, refilled by heating more oxalate, and the gas allowed to stream out through the pump for some time. The heat was then lowered, sparks were passed and the spectrum observed. No trace whatever of the nitrocarbon bands could be detected, however the spark might be varied. The pump was now set going again, and the pressure of the gas reduced to 1 inch of mercury, while the spectrum was observed from time to time. Still no trace of the nitrocarbon bands could be detected. More of the oxalate was next heated, and the observations repeated again and again, always with the same result. We came, therefore, to the conclusion that carbonic oxide, if quite free from nitrogen, does not give, at the atmospheric or any less pressure, the nitrocarbon spectrum.

From Dr. Watts' account of his experiments, it appeared that he had used carbonic oxide prepared by the action of sulphuric acid on ferrocyanide, and it was probable that it might have been contaminated with nitrogen, or with nitrogenous compounds, from the ferrocyanide. We accordingly repeated our experiments with carbonic oxide so prepared, and found that the nitrocarbon bands were then always distinctly seen.

We have also repeated Ångström and Thalén's experiments with the spark between carbon poles in nitrogen and carbonic acid gas. For this we used a wide glass tube (fig. 7), to one end of which a quartz lens, *a*, was cemented, while the other was stopped with a cork, through which were passed two stout platinum wires with little cones of carbon (*b*), purified in Bunsen's manner, fastened, as shown in the figure, on

to their ends. Two narrow glass tubes were also passed through the cork, one reaching the whole length of the bigger tube for the introduction of gas, and the other a short one for exit. The tube was first filled with nitrogen. On passing the spark we observed, as Ångström and Thalén say, that about the poles the nitrocarbon bands were



plainly seen; and they were visible through a great range of variations of the character of the spark; even the use of a condenser of moderate size (a litre flask full of sulphuric acid and coated to the neck with tinfoil) did not diminish them. Photographs were then taken, with and without the use of the condenser, and these showed the violet and ultra-violet nitrocarbon bands including those near N and P. The nitrogen was now swept out by a current of carbonic acid gas, and on now passing the spark the nitrocarbon bands could no longer be detected, and photographs taken as before showed no trace of any of them.

In order further to test the sensibility of the spectroscopic test for nitrocarbon compounds, and the permanence of such compounds under variations in the electric discharge, we drew out, so as to form long narrow necks, both ends of a glass tube of 110 cub. centims. capacity which had wires sealed into it in the same way as before, and into one of these necks we introduced a minute quantity, .002 grm., of mercury cyanide; a current of hydrogen was then passed through the tube at atmospheric pressure, and when it was judged that the air must be thoroughly expelled, the tube was closed by the blowpipe. On passing the spark no trace of nitrocarbon bands could be seen. The mercury cyanide was then heated to decomposition by a spirit lamp. The nitrocarbon bands immediately made their appearance, and were well, even brightly seen, and they did not disappear when a strong spark from a very powerful induction coil was passed, or even with the use of a condenser consisting of two such flasks as are above mentioned. There was no sign of any permanent decomposition of the cyanide; the bands continued to show well after the passage of the spark had been maintained for a long time. The whole quantity of cyanogen which the amount of cyanide introduced would give if it were wholly decomposed, which is not the case at the temperature employed, is less than $\frac{1}{600}$ of the volume of the whole tube, *i.e.*, of the hydrogen with which it was mixed.

It appears from this experiment not only that the test is an extremely

sensitive one for nitrocarbon compounds, but that cyanogen is far more permanent under the electric discharge when mixed with a large bulk of hydrogen than when the discharge is passed through cyanogen alone.

In all the foregoing experiments the bands which Ångström and Thalén ascribe to hydrocarbons were always more or less plainly seen; and we have come to the conclusion that much more care than has generally been thought necessary is needed if the last traces of hydrogen and its compounds are to be removed from spectral tubes. Indeed, we do not think that all water can be removed from apparatus and reagents which do not admit of being heated to redness. To illustrate this, we may mention one or two experiments.

Into the bulb of a sparking tube similar in form to that of fig. 4, but rather longer, some loose phosphoric anhydride was introduced and then some well dried and redistilled carbon bisulphide. The end of the tube having then been drawn out the carbon bisulphide was boiled out in an oil-bath at a temperature of 200° C., and the tube sealed off. On passing the spark without condenser the hydrocarbon bands were discernible, and on putting on the condenser the hydrogen line C came out plainly and was identified by comparison with an ordinary vacuum tube containing hydrogen. One would have supposed that the phosphoric anhydride would have retained all the moisture, and that there could be no other source of hydrogen in the tube.

In another experiment a mixture of carbonate of sodium and boric anhydride, previously to admixture heated red hot, was introduced into one end of a piece of combustion tube, near the other end of which wires had been sealed, and the open end drawn out; the mixture was then heated, and when it was judged that all the air was expelled, the tube was sealed off at atmospheric pressure. On passing sparks through it carbonic oxide bands and oxygen lines could be seen, but no hydrogen, hydrocarbon, or nitrocarbon bands could be detected. It appears, therefore, that the application of a red heat is likely to prove a more effectual means of getting rid of moisture than the use of any desiccating agent.

The first point we have had before us in these investigations is whether the groups of shaded bands seen in the more refrangible part of the spectrum of a cyanogen flame, of which the three which can be detected by the eye are defined by us in our previous paper on this subject by their wave-lengths (4600 to 4502, 4220 to 4158, and 3883 to 3850), are due to the vapour of carbon uncombined, or, as we conclude, to a compound of carbon with nitrogen.

Now, the evidence that carbon uncombined can take the state of vapour at the temperature of the electric arc is at present very imperfect. Carbon shows at such temperatures only incipient fusion, if so much as that, and that carbon uncombined should be vaporised at the far lower temperature of the flame of cyanogen is so incredible an

hypothesis, that it ought not to be accepted if the phenomena admit of any other probable explanation. On the other hand, we have shown that cyanogen or hydrocyanic acid is generated in large quantity in the electric arc taken in nitrogen, and Berthelot has shown that hydrocyanic acid is produced by the spark discharge in a mixture of acetylene and nitrogen, so that in the cases in which these bands shine out with the greatest brilliance, namely, the arc in nitrogen and the cyanogen flame, we know that nitrocarbon compounds are present. Further, we have shown that these bands fade and disappear in proportion as nitrogen is removed from the arc. Ångström and Thalèn had previously shown the same thing with regard to the discharge between carbon electrodes; and the conclusion to which they and we have come would probably have commanded universal assent if it had not been for the fact that these bands had been seen in circumstances where nitrogen was supposed to be absent; but where, in reality, the difficulty of completely eliminating nitrogen, and the extreme sensibility of the spectroscopic test, had been inadequately apprehended.

To clear up the question from this point of view, the experiments now detailed have been made, and they appear to us quite conclusive. Were the evidence less conclusive than it is, it would still be as rash and as illogical to conclude from the appearance of the nitrocarbon bands in a case where nitrogen was presumed, not proved, to be absent, that they were not due to a nitrocarbon, as it would be to deny that the well-known yellow lines were due to sodium, because they had been seen in cases where sodium was supposed to be absent. Our argument is an induction from a very long series of observations which lead up to one conclusion, and hardly admit of any other explanation. But Mr. Lockyer attempts to explain the disappearance of the bands when nitrogen is absent, by the statement, "that the tension of the current used now brings one set of flutings into prominence, and now another." This is no new observation. It is well known that variations in the discharge produce variations in the relative intensities of different parts of a spectrum. Certain lines of magnesium, cadmium, zinc, and other metals, very brilliant in the spark, are not seen, or are barely seen, at all in the arc. His remark might be applied to the spectra of compounds as well as to those of elements. Variation in the discharge accounts very well for some of the variations of intensity in the bands if they be due to a nitrocarbon; it will not, however, account for the fact observed by us, that the bands, or those of them which have the greatest emissive power, and are best developed by the particular current used, come out on the addition of a minute quantity of nitrogen, when there is every reason to think that no variation of the current occurs. *

* It is worthy of note, that if we number the sets of bands of the spectrum of hydrocarbons, beginning with the orange set, and those of cyanogen, beginning with

Much the same may be said with regard to the changes of the spectrum produced by changes of temperature. We cannot infer from any of these changes that the spectrum is not due to a compound. The bands in question are singularly persistent through a great range of temperatures, from the temperature of a cyanogen flame cooled by admixture with carbonic acid gas, as related by Watts ("Phil. Mag.," 1869, p. 258), to that of the spark of an induction coil with condenser.

But again, Mr. Lockyer attempts to get over the difficulties of his case by the supposition that "the sets of carbon flutings represent different molecular groupings of carbon, in addition to that or those which give us the line spectrum."

Now, until independent evidence that carbon can exist at all in the state of vapour uncombined at the temperature of a cyanogen flame can be adduced, and further independent evidence of the existence of different groupings in such vapour, the hypothesis here enunciated is a gratuitous one, so long as any other hypothesis for which independent evidence can be adduced, as is true of the existence of nitro-carbon compounds in the flame, arc, and spark, will sufficiently explain the facts.

Whether or no the nitrocarbon bands are visible in the solar spectrum is not in dispute, for we have never hitherto expressed any opinion on that point. The observation above recorded, that there is in the spectrum of cyanogen a strong shaded band coincident with the very characteristic dark shaded band P, strengthens materially the evidence in favour of the existence of these bands in the solar spectrum; the more so, as the series of lines at P has far more of the distinctive character of the cyanogen spectrum than any other series in the ultra-violet part of the solar spectrum.

However that may be, we contend against the hypothesis that if present they can be due to any vapour of carbon uncombined in the upper cooler region of the chromosphere. One object of our investigations has been to determine the permanence of compounds of non-metallic elements, and the sensitiveness of the spectroscopic test in regard to them. It appeared probable that if such compounds existed in the solar atmosphere their presence would be most distinctly revealed in the more refrangible part of the spectrum, and this is a subject with which we purpose to deal in a further communication. In the meantime it is sufficiently clear that the presence of nitrogen in the solar atmosphere may be recognised through cyanogen when free nitrogen might escape detection.

In a footnote of his paper Mr. Lockyer assigns the wave-length 3881

the least refrangible of those shown in our diagram, fig. 1, then the most persistent in the hydrocarbon flame-spectrum are 2 and 5, while in the visible part of the spectrum of cyanogen they are 3 and 4, but there are conditions of the nitrocarbon spectrum in which the three lines near G seem to be most persistent.

as approximately that of the least refrangible edge of the ultra-violet set of bands next above K, whereas in our former paper we had given it as 3883·5. Now, as we have before explained, we have never set ourselves to the exact determination of wave-lengths, we have rather used them as convenient handles by which to designate particular lines; but a repetition of the measures of our photographs does not confirm Mr. Lockyer's number. The photographs were those of the arc from a De Meritens machine in one of our lime crucibles, and gave the iron lines well developed; and we used the iron lines, wave-lengths 3906, 3902, 3898·5, 3894·8, and the pair between 3877 and 3878 as lines of reference. These measures give, as a minimum, the wave-length 3882·7. In Cornu's map a manganese line is given with the wave-length 3881. None of our photographs show this line, though manganese was purposely introduced into the crucible, and the other manganese lines came out well and strong. We should not put a determination made in this way against a direct determination of the wave-length by a diffraction grating; but unless there be an error in the identification of the iron lines, or Cornu's wave-lengths for those lines be erroneous, neither of which suppositions is at all probable, we conclude that the wave-length is more nearly 3883 than 3881. If this be correct, the band covers a markedly luminous portion of the solar spectrum as shown in Cornu's map.

Mr. Lockyer has forced us to go again over some of the ground which we had previously traversed, by making such a statement as the following:—

“I have therefore thought it desirable to go over the ground again, modifying the experimental method so as to demonstrate the absence of impurities. Indeed, I have started upon a somewhat lengthy research, and have taken a large number of photographs under various conditions, so that to reduce them all will be a work of time. I beg permission, therefore, in the meantime, to submit to the notice of the Society an experiment with a tube containing CCl_4 , which, I think, establishes the conclusions arrived at by prior investigators. And I may add that it is the more important to settle the question, as Messrs. Liveing and Dewar have already based upon their conclusions theoretical views of a kind which appear to me calculated to mislead, and which I consider to have long been shown to be erroneous.”

As we have now demonstrated the utterly unsatisfactory character of the crucial experiment on the strength of which Mr. Lockyer condemns in so sweeping a manner our conclusions, it is unnecessary to add any further comment.*

* Mr. Lockyer has communicated to the Society a “Further Note on the Spectrum of Carbon,” since the above was written. We see no reason to modify our conclusions regarding the carbon spectrum on account of any new facts brought forward. The discussion of the paper we leave until a future occasion.

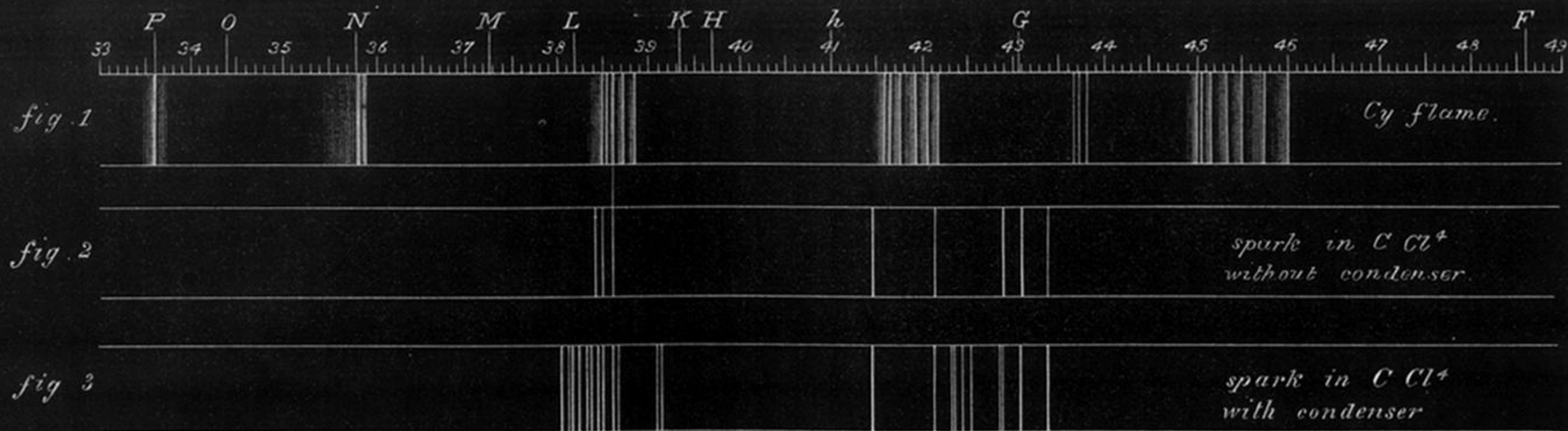
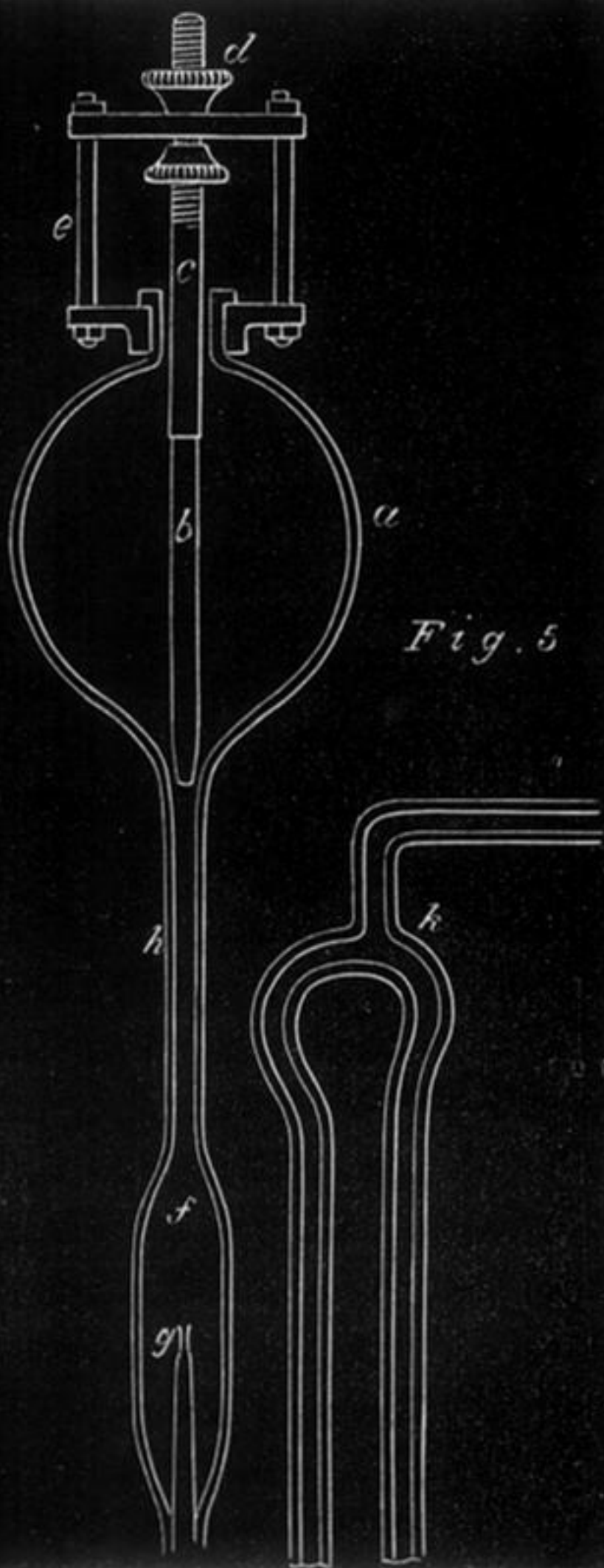


Fig. 4





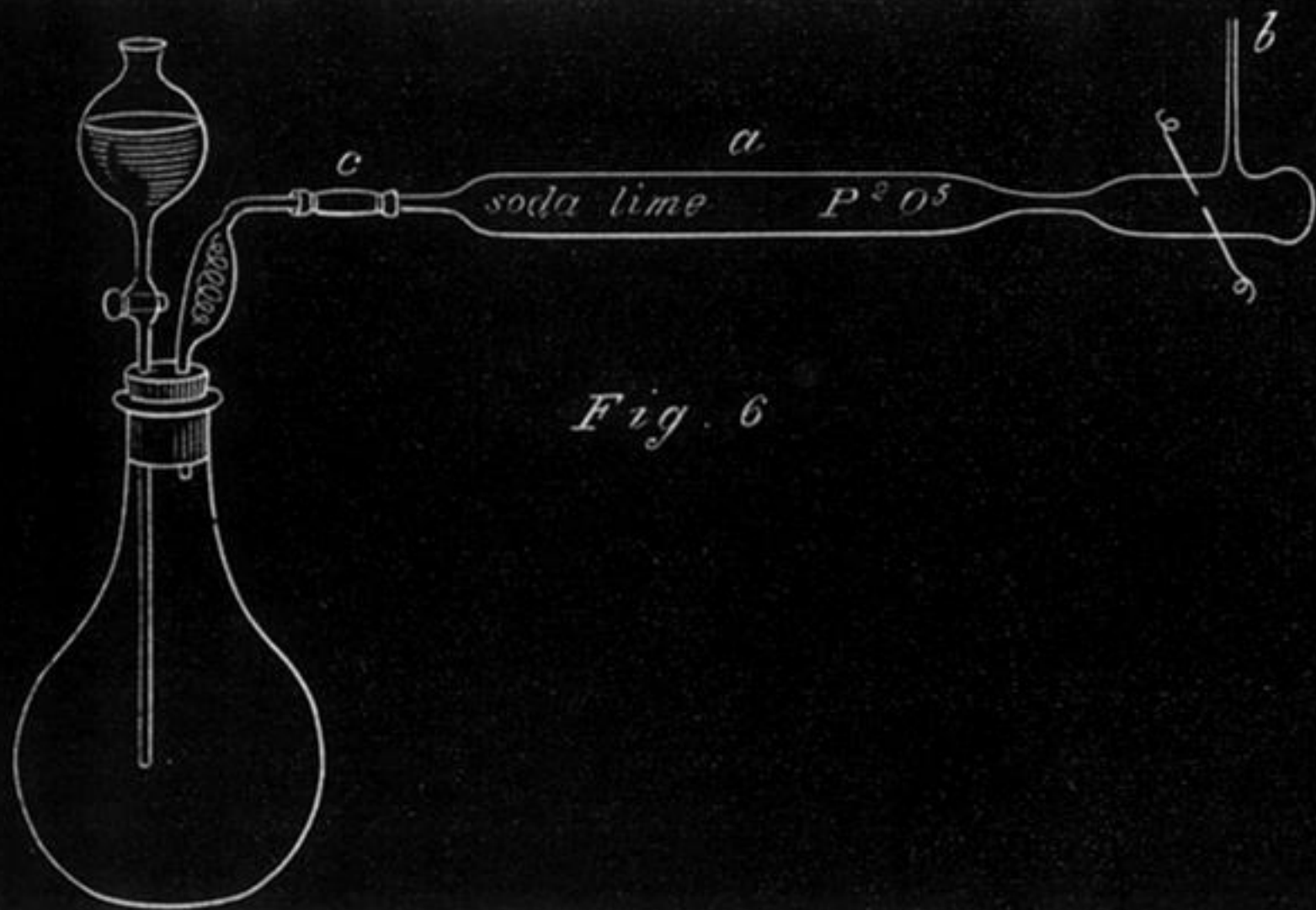


Fig. 7

